On the Thermo-chemistry of Flame Spectra at High Temperatures.

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The majority of the metallic elements have two distinct spectra, one of lines, the other of bands. In some spectra, bands are the most prominent feature in association with but few lines; in others the lines predominate over the bands. Of those substances with bands in their spectra there are many which may be reduced in quantity to almost a minimum without the bands disappearing from the flame or from the uncondensed spark; from this it would appear that there is a very intimate relationship between the bands and lines of the same element. It has been supposed that such bands as cannot be attributed to definite salts are the spectra of oxides or even of hydrides, but many facts have been accumulated from which it is evident that this is not correct. On the other hand, many of the elements which possess complex molecules may readily be understood to emit molecular or band spectra, but some further explanation is necessary when the molecule of the element is monatomic.

The present communication deals only with one part of this subject, being merely a record of observations on high temperature flame reactions, and principally those of the alkali and alkaline earth metals. The spectra of the alkali metals at the highest temperature in the flame of the oxyhydrogen blow-pipe more nearly resemble those obtained from the arc than any other spectra of the same elements. Thus, all the lines of lithium photographed by Kayser and Runge in the arc have been obtained in the flame from lithium nitrate. This is evidence of the high temperature obtainable in the flame, but if further evidence were desired, we have it in the great facility with which both gold and silver can be vapourised and condensed from the vapour, the large number of arc lines of iron, practically all those that are reversible, which appear in the flame, and the volatilisation of palladium and iridium in weighable quantities.

Part I.—Band Spectra of the Alkali and Alkaline Earth Metals.

Lenard[*] has recently described the coloured glow emitted by globules of fused salts in the Bunsen flame, the particular parts of the flame from

[*] 'Annalen der Physik,' 1905 (IV), vol. 17, pp. 197—247.

which the glow emanates, with the spectrum of the glow from different metals.

The spectra of the glow from metallic vapours have been photographed repeatedly in the oxyhydrogen flame spectra of all the alkali metal salts,[*] and those of the alkaline earths, but Lenard states that he has not been able to find the maximum of brightness of the continued rays of potassium, at or near λ 5500, as it appears on the reproduction of my photographs (Plates 6 and 7). On referring to the plate, I do not see that the maximum is at λ 5500, and the strong continuous rays are so evenly distributed over so wide a range of spectrum that it is better to refer to the letterpress of the publication.

The continuous spectrum of lithium extended from about λ 4600 to λ 3200 ; of sodium very strongly from λ 6020 to λ 3600 and continued weakly to λ 3320 ; of potassium it was intense from about λ 4600 to λ 3400, but continuous rays were observed from about λ 5700. As importance has been attached to the kind of photographic plate used, it is as well to state that isochromatic plates of Edwards', or of the Ilford make, and Cadett and Neall's spectrum plates, were most generally in use, but when the plates were not isochromatic, the fact was recorded on the photograph. On the photograph referred to by Lenard, the plate was less sensitive to the green than to the orange and red rays, so that a weak space is seen between λ 5359 and λ 5200. The continuous spectra have been carefully examined on more than 40 different photographs of the alkali-metal salts, including sulphates, nitrates, carbonates, and chlorides; also potassium cyanide, ferrocyanide, ferricyanide, and fluo-silicate.

A hitherto undescribed feature in the spectra which is unquestionably due to each metal, is the occurrence of a multitude of bands in the rays of lithium, sodium, and potassium, which occupy spaces within the above-quoted wave-lengths.

The photographed spectra of potassium chloride, as emitted by different flames, were studied. In no case did the nature of the salt, the support used, or the nature of the flame, make any difference, except in lengthening or shortening the exposure which, *during comparatively short periods*, was proved to have the same effect as putting more or less of the salt into the flame.

It is deemed of importance that this should be recorded, because different metals, and also different salts of the same metal, under the same conditions show different results, and this arises principally from the difference in

* "Flame Spectra at High Temperature," 'Phil. Trans.,' 1894, vol. 185, A, pp. 161—212.

volatility of the salts, or the comparative ease with which they are thermo-chemically decomposed. It is also important that the salts be pure, otherwise the spectrum of one may interfere with the other, the two spectra become confused, and the bands are not visible.

Lithium Salts.—Various specimens of the sulphate, carbonate, chloride, and nitrate, were used, but most of the spectra were photographed from the nitrate. Latterly the salts obtained have been so pure that the sulphate showed hardly a trace of any other metal, even sodium, and no calcium.* They show all the lines attributed to lithium by Kayser and Runge. The structure of the background is that of fine lines and very narrow bands extremely close together, extending from $\lambda\,3466$ to $\lambda\,4677$. But it must be observed that a feeble group of the water-vapour lines may be seen on other spectra extending to $\lambda\,3466$, therefore to be sure that these may not be mistaken for lithium bands, it is better to place the margin of the latter below $\lambda\,3610$ and to disregard the rays of greater refrangibility. The lithium bands, therefore, without doubt, extend from $\lambda\,3610$ to $\lambda\,4677$. The lithium spectrum, exclusive of the lines, is a very weak one, so that an extended band of continuous rays is more often photographed than a discontinuous spectrum consisting of a multitude of fine lines and narrow bands.

Sodium Salts.—The banded spectrum of sodium has been observed on three photographs, but it is only feebly visible. A complete array of the bands was photographed from very pure rock salt, and from a specially prepared pure sodium chloride. Like the lithium bands, they are very narrow and close together; they extend from rays a little less refrangible than $\lambda\,3700$ down to about $\lambda\,4800$. A beautiful banded spectrum has recently been photographed from sodium carbonate in the oxyhydrogen blow-pipe flame. Some feeble lines accompany the bands, and the principal lines D^1 and D^2 are enormously extended on each side so as to form a broad band. O. H. Basquin observed a series of lines in the spectrum of the sodium arc when surrounded by an atmosphere of hydrogen; they lie between $\lambda\,5000$ and 3800.† "This is probably a complicated fluting of heads of bands, less clearly marked than usual, and running towards shorter wave-lengths." It is more than probable that the bands which I have observed are of the

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* These salts were kindly presented to me by Mr. W. E. B. Blenkinsop, the Managing Director of the firm of May and Baker, Ltd., of Garden Wharf, Battersea, London.

† 'Astrophys. Journ.,' 1901, vol. 14, p. 1. In lieu of any better hypothesis, Basquin supposed that the banded spectra of several of the metals, including sodium, are due to hydrides being formed in the arc. Sodium hydride cannot exist in a state of vapour; it readily undergoes dissociation, which commences at 200° and is complete at 422°, under ordinary barometric pressures; the bands, therefore, are not due to sodium hydride.

same nature as those which he, by the aid of a large concave grating, resolved into lines.

There is an important difference between the spectrum of sodium taken from the metal when burnt in a Bunsen flame and that obtained in the oxyhydrogen blow-pipe flame, but it appears to be due solely to the lower temperature of the former. With metallic sodium, no lines but the principal yellow ones are visible, these are very broad and dense. It is extremely difficult to introduce sodium into the oxyhydrogen blow-pipe flame, because it melts so readily and escapes. The sodium spectrum from salts gives not only the D^1 and D^2 lines more widely extended on either side than is the case with the metal, but also the subordinate series of lines, the band of continuous rays, and with the highest temperature of the flame, the series of bands in these rays in addition.

Potassium Salts.—The potassium bands are very easily photographed from many different salts. They are themselves wider, and also wider apart than those of lithium and sodium, and the structure of the banded spectrum varies greatly with the quantity of the substance used, and with the exposure given. Many lines accompany the stronger banded spectrum.

The potassium bands, as obtained from weighed quantities of potassium chloride, frequently extend from $\lambda\,3600$ to $\lambda\,4800$. This effect is obtained from 0·05 gramme of the salt, but with 1 gramme or an exposure of 5 minutes, the bands may stretch down into the red. With an exposure of $1\frac{1}{2}$ minutes there is barely an indication of bands, and when the quantity of the chloride is reduced to 0·025 gramme, there is nothing but a continuous spectrum to be seen. Potassium cyanide and ferrocyanide with the same exposure both yielded very dense spectra, but on that account the bands are not seen distinctly. They are well seen in spectra photographed from potash alum, potassium carbonate, and potassium ferricyanide. Between the wave-lengths of two cadmium lines, 4800·8 and 4414·5, ten of these bands were counted. They are not sharp at the edges, and the spaces between successive bands decrease as they tend towards the violet. They appear, in fact, like a continuation of the subordinate series of lines, 4808·8, 4803·8, 4796·8, 4788·8, and 4759·8 (Liveing and Dewar), but they are diffuse. There is an absence of any accompanying fine lines such as are seen in the lithium and sodium spectra. Spectra from sodium and potassium carbonates have recently been photographed with Wratten and Wainwright's panchromatic spectrum plates, which give the lines well defined with the continuous rays from wave-lengths 7699·3 and 7665·6 of potassium to a line 3303·1 which belongs to sodium. There is a strong band in the red, extending from $\lambda\,6911$ to $\lambda\,7350$, fading away rather abruptly on the less refrangible side,

but with feeble continuous rays extending to $\lambda\,7665\cdot6$. The bands mentioned above are seen to be composed of two groups; the one nearer the red appears like the continuation of the subordinate series of lines with the spaces between them decreasing, and the second group more towards the violet, where the bands do not appreciably vary in width or in distance apart.

Rubidium Salts.—Sulphate and chloride of great purity yielded merely a continuous spectrum in which there are no bands, but the lines are very broad and strong.

Cæsium Salts.—The same effect is seen with the corresponding salts of cæsium.

Banded Spectra from the Alkaline Earth Salts.

The banded spectra observed with barium chloride and strontium sulphate are reproduced, but with a dispersion of only one prism on Plate 6, in "Flame Spectra at High Temperatures."* In course of a study of the oxyhydrogen flame spectra of calcium, strontium, and barium compounds, made in 1902, bands were constantly observed in minerals containing barium, just as the bands of lead are constantly seen in the flame spectra of minerals containing lead and, subsequently, the barium bands were photographed from the flame spectra of very carefully prepared compounds which were spectroscopically pure.

The bands in the continuous background of rays are different from those of the alkali metal group. In calcium and strontium the most conspicuous bands are broad and disposed somewhat irregularly, but in detail the spectra of calcium, strontium, and barium compounds show bands of two varieties, the one broad overlying narrow bands; when the quantity of material is small, only the narrow bands are seen, and when the slit is not narrow enough they appear as diffused rays or a continuous spectrum. As in the lithium, sodium, potassium group, the calcium, strontium, and barium spectra differ much in intensity, and follow in the same order as the alkali metals in this respect, which is that of the numerical values of the atomic weights of the metals, the higher the value the greater the volatility of the compound. The strontium and barium chlorides exhibit the banded spectra best, but they are well seen also in sulphates, carbonates, and oxides. The best mineral in which to study the bands of calcium is the natural sulphate, selenite. It should not be overlooked that compounds yield their own spectra, such as chlorides, under certain conditions, phosphates and fluorides, as, for instance, ferrous phosphate and calcium fluoride. The oxides B_2O_3 and P_4O_{10} also emit their own spectra, but

* 'Phil. Trans.,' 1894.

whereas the former shows bands, the latter shows lines only. This has been made the basis of a method of separating alkali metal flame spectra from those of the alkaline earth metals.* Bands characteristic probably of the sulphates may be found to overlie the metal bands.

Several different compounds of barium have all been found to yield the same banded flame spectrum when a sufficient quantity of substance is introduced into the flame, and all strontium salts also yield in like circumstances the same flame spectrum. When the sulphates of the alkaline earths are submitted to the oxyhydrogen flame, they all yield the banded spectra, and in the case of calcium and strontium sulphates, also certain lines in addition, but barium sulphate frequently shows only the bands without the barium line; therefore, the lines appear more readily than the bands with calcium salts, and the bands more readily than the lines with barium compounds. In fact, barium behaves in this respect very much as lead does.

There is an important difference in the chemical nature of the three sulphates after being heated in the flame: thus, the barium sulphate is entirely reduced to sulphide, so that we arrive at the fact that the same spectrum is common to chloride, oxide, and sulphide. But the chlorides are converted by the water-vapour in such a flame into oxides, so that we have simply the oxide and sulphide to consider.

The strontium sulphate is reduced partly to oxide and partly to sulphide under precisely the same conditions, and the calcium salt is simply converted into oxides. As the oxide produced from the chloride and sulphide produced from the sulphate of barium yield exactly the same banded spectrum, it is evident that we are dealing with the spectrum of the only constituent in common, which is the metal. It is quite inconceivable that the oxide and sulphide should give identical spectra of the respective compounds because the molecular weights of the compounds are different. The same observation applies to the compounds of strontium, which yield spectra with lines and bands, but we know that strontium sulphate, after it has been removed from the flame, has by less than one-half been reduced to sulphide; it is, therefore, probable that in this case as in that of barium, the spectrum is caused either by the dissociation of the sulphide in the flame or by a chemical reduction. Calcium sulphate is not simply deoxidised in the flame, like the corresponding salts of strontium and barium, but is converted into lime, yet this compound exhibits both lines and bands.

* 'Chem. Soc. Trans.,' 1893, vol. 63, p. 138.

Evidence of Thermo-chemical Reduction of Refractory Oxides in the Flame.

It has already been shown that aluminium can be reduced from its oxide in the oxyhydrogen flame, that it colours the flame and emits the two lines $\lambda\lambda$ 3967 and 3946. It was concluded that bands which have been attributed to the oxide are in reality metal bands.* Bands of beryllium and lanthanum were also reduced from their oxides; the greater volatility of metallic beryllium[†] caused the band spectrum to be photographed without the lines.

I have now arrived at the conviction, from additional evidence presently to be adduced, that calcium and strontium are also produced in the oxyhydrogen flame by thermo-chemical reduction of their oxides and sulphides.

The question of the reduction of the oxides of the dyad and triad groups is quite different from that of the oxides of the alkali metals, because compounds of the latter are not only easily volatilised, but it has been proved by St. Claire Deville that in the manufacture of the alkali metals, the oxides are thermo-chemically dissociated, and then reduced by carbon entering into immediate combination with the dissociated oxygen.

Spectro-chemical Evidence from Anhydrous Flames and Dehydrated Salts.

By an anhydrous flame is meant one in which water is not a product of combustion. Any salt which yields the spectrum, or imparts the characteristic colour of the metal to such a flame, is excluded from the view of Arrhenius that vapourised salts are first hydrolysed by water-vapour in the flame, that the hydroxides thus formed undergo ionisation, and the spectra are caused by the metallic cations. Smithells, Dawson, and Wilson first applied this test to alkali salts, by heating them in the flame of burning cyanogen.[‡] Lenard also has observed that sodium salts colour the flame of carbon disulphide. The authors aforesaid suggest that a chemical reduction takes place and the metal then colours the flame. I have extended this enquiry by placing anhydrous salts in the flame of carbon monoxide. Smithells has shown that, if this gas be carefully dried, it will not inflame when issuing from a jet, but if the jet be heated the gas ignites. It has also been shown[§] that carbon monoxide stored over water in a gasholder will not inflame in air if the jet be small like that of a Bunsen or ordinary "bat's wing" burner, but it will burn from a tube if the orifice be wide enough,

* 'Banded Flame Spectra of Metals,' p. 346, and Plate XXXI.
† This was observed by Pollok in its reduction by the arc.
‡ 'Roy. Soc. Proc.,' 1899, vol. 64, p. 142.
§ Hartley, "On the Temperature of Certain Flames," 'Chem. Soc. Trans.,' 1896, vol. 69, p. 844.

and even from a " bat's wing " burner when the pressure is small ; though in these latter circumstances the flame is very small. In view of these facts, pure carbon monoxide was most carefully dried, first with a column of pumice saturated with oil of vitriol, and then with two large tubes of phosphoric anhydride.

The gas was conducted into a platinum tube with an internal diameter of 6 mm. and a length of 30 cm. It was found that under these conditions the gas was very difficult to inflame, but it did burn ; nevertheless, to increase the temperature and render the same steady by ensuring combustion, the tube was heated red-hot by a Mecke burner placed 3 inches from its orifice.

On introducing into the flame recently ignited carbonates of lithium, sodium, and potassium, even without heating the platinum tube, beautiful spectra were observed, such as are visible in the flame of a Bunsen burner. It was very difficult to see the red line of potassium about $\lambda\,7660$, but the green glow and a group of green lines about $\lambda\,5800$ were observed. Experiments were tried in both the inner and outer cones, but only when the substance was heated at the tip of the inner cone could the group of green lines be seen. In this instance it is not reasonable to suppose that sufficient water could gain access to the flame to give rise to hydrolysis, and, in fact, hydrolysis could not take place.

The same experiments were repeated with the oxides, carbonates, nitrates of calcium, strontium, and barium ; but although the platinum tube was heated to bright redness, there was no trace of a spectrum of either bands or lines in any case. Calcium, strontium, and barium chlorides, on the other hand, showed superb spectra of the chlorides, apparently identical with those produced by heating the same salts in a coal-gas flame saturated with hydrochloric acid. The temperature of this carbon-monoxide flame, which was from 50 to 75 mm. long, is higher than that of a Bunsen burner of the same size,* and can raise a larger mass of material to a higher temperature.† Here we have evidence that the metals of the alkalies behave quite differently from those of the alkaline earths ; calcium, strontium, and barium chlorides are volatile without decomposition, for they fuse and remain clear liquids without showing turbidity for as long as is necessary to observe their spectra. Inasmuch as they appear to yield their own spectra, they behave like calcium fluoride when placed in the oxyhydrogen blow-pipe flame, and doubtless other similar fluorides and phosphates. The most important facts ascertained so far are, first, the alkaline earth oxides are not

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* *Loc. cit.*

† Platinum wire 1/40th mm. in thickness can be melted into a globule in any part of the flame.

volatile in the carbon-monoxide flame, or, if they are, they show no spectrum; second, the flame is a powerful reducing one to all oxides with a heat of formation not greater than that of zinc oxide, but the oxides in question are not reduced; thirdly, the temperature of the flame is higher than that of a Bunsen burner, and over a large area it is nearly as high as that of the oxyhydrogen flame; fourthly, the chlorides are volatile in an anhydrous flame, but the stability of the chlorides in such a flame is somewhat doubtful, as they may undergo dissociation.

The action of the cyanogen flame is very different from that of the flame of carbon monoxide, because cyanogen is a very powerful reducing agent.

When calcium oxide was introduced on a platinum wire into the flame of cyanogen burning in air, there was no action low down in the flame, but when the substance was placed at the tip of the inner cone, there was a magnificent display of the same spectrum as that seen when calcium metal is burnt in air, and with no trace of the cyanogen bands. The effect on baryta was tested in a similar manner, by making pure barium carbonate into a stiff paste with water, and moulding it round a loop of platinum wire. On placing this in the flame at the same point, an equally fine spectrum of barium was obtained. In both instances the spectra were identical with those photographed when the same compounds were placed in a Mecke burner, but the brilliancy and intensity of the rays were greatly increased.

Beyond all doubt these spectra are the spectra of the metals.

The deductions from these facts are, that the lines and bands seen in the oxyhydrogen flame are certainly not the spectra of the oxides, because if the difference between this and the carbon monoxide flame were simply one of temperature, the emission spectra of oxides and sulphides should be quite as easily produced in a carbon monoxide flame as in one of hydrogen. Finally, carbon monoxide was burnt with oxygen in a Deville blow-pipe and still no spectrum of calcium or strontium was seen, except when traces of chloride were present. The salts were supported on very thin slips of Donegal kyanite.

The presence of hydrogen in the flame is, therefore, a necessary element in some chemical reaction which leads to the reduction of the sulphides or oxides to the metallic state. The temperature of these flames, which can melt platinum, is sufficient to effect the thermo-chemical dissociation of water-vapour, and it is probable that in this lies the cause of the spectra appearing.

Spectra of the metals observed in a carbon monoxide flame on the grandest scale are those which were photographed from the Bessemer "blow," but in this case the spectra are not due to the heating of a substance in a pure gas

or even in a mixture of gases, but are the result of the internal combustion of impurities in the metal, which causes the vapours to be carried off in a stream of intensely heated carbon monoxide mixed with nitrogen and a small proportion of hydrogen, all of which gases, except the nitrogen, are burnt in the air. The average vapour pressure of water in the blast amounts to about 1 *per cent.* of the air; this is reduced by the metal bath to hydrogen and carbon monoxide and, as the temperature is an exceedingly high one, it is not surprising that a line spectrum of calcium seen in the oxyhydrogen flame has been photographed in the Bessemer flame, the flame being a mixed hydrogen and carbon monoxide one. The lines are, however, only two, namely, 4226·9 and 4581·6. Arguments from Bessemer flame observations rather lead to confusion, on account of the many other elements present in the flame, and they must therefore be rejected or treated with discrimination.

It will be observed that in the groups Li, Na, K, and Ca, Sr, Ba, the facility with which the bands are produced increases with the atomic weights, likewise the volatility of metals increases in the same order, and as, in the first group, the elements are monatomic, the relative vapour densities are half their atomic weights; accordingly we have 7/2, 23/2, 39/2 as the relative quantities of matter in the flame if they have all the same volatility and if their oxides undergo dissociation with equal facility; but the least easily dissociated is the least volatile lithium oxide; we may therefore say that the vapour pressure of potassium will be at least six times that of lithium in any flame in which the two oxides are placed under the same conditions. As there is very little difference between the heats of formation of the groups of oxides, CaO, SrO, and BaO, the energy required for their reduction may be considered to be the same for each oxide. The respective volatilities of the oxides or of the metals is not known, neither are we acquainted with their vapour densities; accordingly we may assume them to be either monatomic or diatomic molecules; if the latter, then the relative quantities of vapour in the flame will be in the proportion of the atomic weights, or 40, 87·6, and 137·4; if they are monatomic, half these quantities, which gives three and a-half times as much vapour of barium in the flame as of calcium, under the same conditions in either case. If, however, we attempt to compare the vapour densities of the alkali metals with those of the dyad group as judged by their spectra, we are at once met with a difficulty by the reactions in the flame by which the metals are set free, being different for each group.

Part II.—On the Chemical Reduction of the Alkaline Earth
Sulphates.

For studying the action of gases in the flame on the insoluble sulphates,
the minerals heavy spar, celestine, and selenite were chosen. Pieces of each
measuring about 15 × 15 × 2 mm. were held by platinum forceps in the
oxyhydrogen flame for a definite period, and then dropped into a measured
volume (50 c.c.) of water. The unaltered mineral was insoluble in each case,
but that which had undergone reduction, whether to oxide or sulphide,
dissolved with a strongly alkaline reaction ; the metal in solution was there-
fore determined volumetrically with standard acid. From the dissolved salts
obtained from heavy spar, sulphuretted hydrogen was evolved in large
quantity, somewhat less in the case of celestine, and hardly a trace with
selenite. The following tabulated statement shows the results obtained :—

	Anhydrous salt.			
	$CaSO_4$.	$SrSO_4$.	$BaSO_4$.	
Time in flame	15 mins.	15 mins.	10 mins.	15 mins.
Metal in solution ...	0·0436 grm.	0·1150 grm.	0·1055 grm.	0·1820 grm.
Metal as sulphide ...	Practically none	10 per cent.	Practically all.	

If numbers be taken proportional to the above quantities, they are found
to be approximately in the ratio of the atomic weights of the elements,
thus :—

$$0·0436 \text{ gramme} : 0·115 \text{ gramme} : 0·182 \text{ gramme} = 34 : 88 : 139$$
$$Ca \quad : \quad Sr \quad : \quad Ba \quad = 40 : 87·5 : 137$$

A sample of celestine was heated in the flame for 35 minutes and dropped
into water, acidified with acetic acid, and the sulphuretted hydrogen precipi-
tated as lead sulphide which was filtered off, converted into lead sulphate and
weighed. The excess of lead was removed and the excess of strontium
determined as carbonate.

Weight of lead sulphate ...... 0·0314 gramme.
Strontium as SrS .... 0·0091 „
Strontium carbonate .... 0·1718 „
Strontium as SrO .... 0·1022 „

These figures show that 8·1 per cent. of the strontium in solution is in the
state of sulphide.

The quantity of strontium reduced from sulphate in 35 minutes was
0·1022 gramme, whereas that reduced in 15 minutes was 0·115 gramme,
or the longer period in the flame has yielded the smaller product.

The Reduction of Barium Sulphate to Sulphide by Hydrogen.

A current of dry hydrogen was passed over a weighed quantity of precipitated dried barium sulphate, heated to redness in a platinum tube. It was soon observed that sulphuretted hydrogen was evolved, probably according to the equations following :—

$$(1) \quad BaSO_4 + 4H_2 = BaS + 4H_2O.$$
$$(2) \quad BaS + H_2O = BaO + H_2S.$$
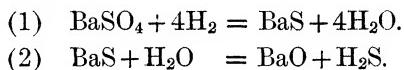
Sulphuretted hydrogen was still being evolved after a period of eight hours, when the experiment was stopped.

$BaSO_4$, initial weight............	0·3226 gramme	= Ba	0·1897 gramme.
$BaSO_4$, residue unchanged ...	0·0059 ,,	= Ba	0·0035 ,,
Difference, substance reduced	0·3167 ,,	= Ba	0·1862 ,,
$PbSO_4$ from BaS, found	0·2822 ,,		
Ba in BaS, found	0·1276 ,,		
Ba in BaO, found	0·0586 ,,		
Total Ba in $BaSO_4$ reduced ...	0·1862 ,,		

The reduced $BaSO_4$ is thus seen to have been composed of BaS = 0·1574 gramme, and BaO = 0·0654 gramme; or about two-thirds sulphide and one-third oxide.

There can be no doubt that the initial action of the hydrogen is the reduction of the sulphate to sulphide, and that probably the whole of the sulphate is reduced; the secondary action, whereby the sulphide is converted into oxide with evolution of sulphuretted hydrogen, is slow and gradual with the barium compound, but takes place with greater facility with strontium, and with completeness in the case of calcium.

When heated to bright redness in a platinum tube through which a current of nitrogen and of carbon dioxide is passed, barium sulphate in neither instance undergoes any change.

When submitted to a white heat in a platinum tube at a reduced pressure for 15 minutes, barium sulphate evolved no oxygen and the substance showed no alkalinity and was quite unchanged.

These experiments show that the hydrogen of the flame is the reducing agent by which the spectra are produced.

Part III.—THE THERMO-CHEMISTRY OF THE REDUCTION PROCESSES IN FLAME REACTIONS.

In studying the thermo-chemistry of flames, it is necessary to consider three separate questions :—

(1) The effect on compounds of high temperatures solely.

(2) The chemical action of other reacting substances in the flame gases on the compound in the flame.

(3) The combined effect of high temperatures and reducing gases.

The thermo-chemical notation used is that of Dr. James H. Pollok.* The solid, liquid, gaseous, and dissolved states are indicated where necessary by a dot, dash, T, or circle ($\cdot$ **—** **T** **O**), placed below the formula of the substance. The heat evolved in the formation of a compound is indicated by ξ placed before its formula, which signifies *energy*.

The heat of a reaction is indicated by enclosing the equation in brackets and placing ξ before it. K° signifies a kilogramme degree of heat, or large calorie, k° similarly is a gramme degree of heat, or small calorie.† The chemical formula for a substance means, as is usual in this connection, its gramme-molecular weight.

In discussing the process of hydrolysis of alkaline chlorides in the flame, we must take into account the following values and place the reaction at a temperature approaching 2000°, then

$$\xi HCl = 26 \ K^\circ \quad \text{and} \quad \xi H_2O = 50\cdot6 \ K^\circ.$$
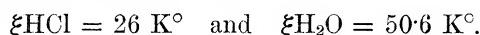
The heat of formation of solid potassium and sodium hydroxides is thus represented—

$$\xi(K + H + O = KOH) = 104\cdot6 \ K^\circ;$$

similarly,

$$\xi NaOH = 102\cdot7 \ K^\circ.$$

The hydrolysis is then

$$\xi(KCl + H_2O = KOH + HCl) = -25\cdot7 \ K^\circ.$$
$$105\cdot7 \quad 50\cdot6 \quad 104\cdot6 \quad 26$$
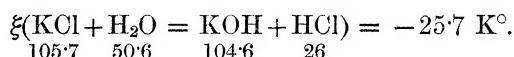
The corresponding value for NaOH is $-19\cdot8 \ K^\circ$.

These reactions are not very strongly endothermic and therefore may occur, and are reversible.

Among the common salts of lithium the sulphate has the greatest stability, nevertheless in a gas flame it is reduced to oxide. Fused lithium sulphate was found to be a perfectly neutral substance, but when a bead of the salt had been heated in the flame of a Mecke burner for an hour it yielded a strongly alkaline solution which did not evolve sulphuretted hydrogen when acidified, nor did it effervesce. It therefore contained the oxide. On taking a larger mass and heating it on kyanite in the oxy-coal-gas blow-pipe flame, care being taken that there should be no free carbon, the

* 'Sci. Proc. Roy. Dublin Society,' 1899, and 'Chem. Soc. Trans.,' 1904, vol. 85, p. 603.

† For the convenient symbol g° C., or gramme degrees Celsius, instead of heats units, or calories, and kilogramme degrees of heat, K° C., we are indebted to Mr. J. Y. Buchanan, "On Steam and Brines," 'Trans. Roy. Soc. Edin.,' 1894, vol. 39, Part III, pp. 529—573.

fused salt became reduced to sulphide. From this it appears that the normal process of reduction of the sulphates in the flame is that given in the two equations referring more particularly to barium sulphate. The difference in the heat of formation of lithium oxide and sulphide respectively, $\xi \, Li_2S = 115\cdot4 \, K^\circ$ and $\xi \, Li_2O = 141\cdot2 \, K^\circ$; this shows how readily the former may be converted into the latter by the action of water-vapour, $\xi \, H_2O = 69 \, K^\circ$, by reason of its being an exothermic action.

The flames from coal-gas, hydrogen, and carbon monoxide respectively, when burning in air, have a temperature as high as that of the melting point of platinum, 1775° C. This temperature exceeds that of the metallurgical furnaces, in which sodium, potassium, cadmium, zinc, and magnesium are reduced and distilled on an industrial scale.

In the manufacture of sodium and potassium from the respective carbonates by means of carbon, the oxide is vapourised and chemically dissociated, thus $Na_2O = 2Na + O$, but the action is not reversible, owing to the presence of carbon, which immediately forms carbon monoxide with the oxygen, thus—

$$\xi(C + O = CO) = 29\cdot4 \, K^\circ \quad \text{and} \quad \xi(CO + O = CO_2) = 68\cdot3 \, K^\circ;$$

therefore, on the whole we have

$$\xi CO_2 = 97\cdot4 \, K^\circ.$$

But $\qquad\qquad \xi Na_2O = 100\cdot2 \, K^\circ \quad \text{and} \quad \xi K_2O = 98\cdot2 \, K^\circ,$

so that where the carbon is oxidised to carbon monoxide only, we have a considerable endothermic action, thus—

$$\xi(Na_2O + C = CO + 2Na) = -71\cdot4 \, K^\circ, \text{ endothermic.}$$

Although this equation does not take into account the fact that the Na_2O is already dissociated, this endothermic action may easily tend towards an exothermic character by the further combustion of the carbon monoxide to carbon dioxide, thus—

$$\xi(2Na_2O + C = 4Na + CO_2) = -102\cdot8 \, K^\circ,$$
$$\underset{200\cdot4}{} \qquad\qquad \underset{97\cdot6}{} \quad \underset{\text{Endothermic}}{}$$

or for one atom of oxygen $\qquad -51\cdot4 \, K^\circ.$

If we suppose the operation to be a simple one of reduction, we have—

$$(Na_2CO_3 + 2C = 2Na + 3CO) = -82\cdot6 \, K^\circ.$$
$$\underset{270\cdot8}{} \qquad\qquad \underset{29\cdot4 \times 3}{}$$

The reduction of K_2CO_3 in like manner would result in an endothermic value of $-90\cdot6 \, K^\circ$. The same reasoning does not apply to lithium oxide, for all attempts to obtain lithium by a similar process of reduction have entirely failed. The reason is, that lithia more nearly resembles the alkaline earth oxides in its chemical properties; it is also the least volatile and least fusible

of the alkali group; moreover, the energy required for its reduction is greater than that necessary for potassium or sodium.   Thus

$$\xi Li_2O = 141.2 \ K° \quad \text{and} \quad \xi Na_2O = 100.9 \ K°.$$

An important fact may be observed here, namely, that whereas the banded spectrum of potassium is comparatively easy to obtain, that of lithium is. very difficult, more difficult than that of sodium, and even the continuous rays are very weak.   The same must be said of rubidium, with the additional remark that its band spectrum has never yet been seen.*   This, undoubtedly, in part arises from the high value for the heat of formation of the oxides of these metals, and it is obvious that these particular properties of lithium serve to explain why the continuous glow observed by Lenard in the case of lithium is weaker than that of either sodium or potassium, which led him to remark that it was probably a property peculiar to that element.   Even rubidium carbonate was reduced by mixing with carbon and heating to a particularly high temperature (Bunsen), but the greater volatility of rubidium compounds may facilitate their dissociation.

It is quite evident, then, that with the fusible and volatile oxides of sodium, potassium, and rubidium, reduction can be effected at a temperature not exceeding a white heat and probably about 1400° C., certainly below the temperature of melting platinum, and below the highest temperatures of the coal-gas, the hydrogen, and the carbonic oxide flames.

Hence I conclude that the banded spectra of lithium, sodium, and potassium observed at the temperature of the oxyhydrogen flame are the spectra of the metals.

The Alkaline Earths.

It has been shown that these substances are of a different nature and their salts are sharply divided into two classes, the haloid and the oxy-salts, each with a different behaviour.

The Haloid Salts.—These are volatile in flames supplied with the halogen hydrides without decomposition.   They are also volatile without decomposition in a dry carbonic oxide flame.   Here, then, we may probably have the spectra of salts and not of the metals.   In a hydrogen or coal-gas flame the salts are hydrolysed and converted into oxides by heat; this is a fact well known.   If we examine the heat of formation of the chlorides, we find it to be, for calcium and strontium respectively,

$$\xi CaCl_2 = 169.9 \ K° \quad \text{and} \quad \xi SrCl_2 = 184.7 \ K°,$$

* A note appears on one of my photographs that there are just faint indications of bands in the strong continuous spectrum.

while the oxides are

$$\xi\text{CaO} = 131\cdot5 \text{ K}° \quad \text{and} \quad \xi\text{SrO} = 131\cdot2 \text{ K}°.$$

The barium chloride has not been determined, but the oxide is

$$\xi\text{BaO} = 133\cdot4 \text{ K}°,*$$

and we may therefore safely say that the energy of formation of the chloride does not differ much from the number deduced from strontium chloride or about 187 K°.

The effect of water-vapour in the flame is an endothermic reaction when the chloride is a solid.

$$\xi(\text{CaCl}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{HCl}) = -37\cdot5 \text{ K}° ;$$
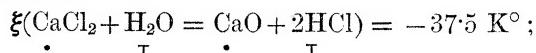
and where towards 2000° C.,

$$\xi\text{H}_2\text{O} = 50\cdot6 \text{ K}° \quad \text{and} \quad \xi\text{CaO} = 131\cdot5 \text{ K}°.$$

The corresponding value for SrCl_2 is $-52\cdot1$ K°. When the chlorides are vapourised in the flame, these endothermic values must be much less and the reactions are easily reversed, as we know by experience when gaseous hydrochloric acid or much ammonium chloride is passed into the flame. We can see clearly also why it is that the carbonic oxide flame does not decompose these salts, the heat of combination of the chlorides being much in excess of that of the oxides, and the reducing power of carbonic oxide, which is the converse of the energy of formation of carbon dioxide, much less, thus :—

$$\xi(\text{CO} + \text{O} = \text{CO}_2) = 68\cdot3 \text{ K}°.$$

It is different with cupric chloride, as this in time is reduced to copper.

The Oxy-salts.—These are all resolved into either oxides or sulphides, or mixtures of the two, when heated in the oxyhydrogen flame. The energy of formation of the oxides is as follows :—

$$\xi\text{CaO} = 131\cdot5 \text{ K}°, \quad \xi\text{SnO} = 131\cdot2 \text{ K}°, \quad \text{and} \quad \xi\text{BaO} = 133\cdot4 \text{ K}°,$$

there being very little difference between them, but these values are all below those of lithium and rubidium, where

$$\xi\text{Li}_2\text{O} = 141\cdot2 \text{ K}° \quad \text{and} \quad \xi\text{Rb}_2\text{O} = 165\cdot4 \text{ K}°.$$

We have now to take into consideration the reducing power of hydrogen at high temperatures in flame reactions. There are two values for the production of gaseous water, the smaller of which is at a temperature approaching 2000°, which we may consider to be the highest temperature of all flames capable of melting platinum—

$$\xi\text{H}_2\text{O} = 58\cdot1 \text{ K}° \quad \text{and} \quad \xi\text{H}_2\text{O} = 50\cdot6 \text{ K}°.$$

* A. Guntz, 'Comptes Rendus,' 1903, vol. 136, p. 1071.

The decreasing value at high temperatures is evidence of the dissociation of water-vapour, which we know does occur at the temperature of white hot platinum. Now both the above values are below that obtained by the combustion of carbon monoxide.

$$\xi(CO + O = CO_2) = 68\cdot2 \text{ K}^\circ ;$$
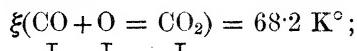
it is, therefore, unnecessary to consider a coal-gas flame apart from one fed with hydrogen, for many of the reductions and dissociation phenomena that can take place in the latter may occur in the former.

The high temperature tends to the dissociation of other oxides than water, and the alkaline earths are most certainly volatilised in Deville's blow-pipe flame, whether they are first dissociated or not. Furthermore, reduction processes are carried on in the solid material, which have not hitherto been suspected, such as the reduction of strontium and barium sulphates to sulphides and of beryllia and alumina to the state of metal.

In the metallurgical process of zinc distillation, the presence of carbon mixed with the ore is necessary. The energy of formation of zinc oxide is $\xi ZnO = 84\cdot8$ K$^\circ$. Supposing the reduction to take place through the medium of carbon monoxide, we have the following :—

I. $\xi(ZnO + C = Zn + CO) = -55\cdot4$ K$^\circ$.
II. $\xi(ZnO + CO = Zn + CO_2) = -16\cdot5$ K$^\circ$.
$$84\cdot8 \quad , \qquad\qquad 68\cdot3 \text{ Endothermic.}$$
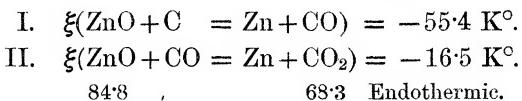
In this case we are considering a solid oxide, not one in the state of vapour; nevertheless we know that reduction does occur though the reaction is endothermic. By recent observations it has been shown that zinc oxide is vapourised at 1400° and rapidly at 1700° C.* and this must greatly facilitate the reduction process.

The reduction of cadmium is more easily accomplished than that of zinc, and hence the cadmium distils over first. The obvious reason for this is that the heat of formation of the oxide is about 21 K$^\circ$ less than that of zinc oxide and $\xi CdO = 65$ K$^\circ$; we have, then, the following equation :—

$$\xi(CdO + C = Cd + CO) = 3\cdot2 \text{ K}^\circ.$$
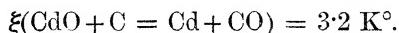
The reduction of cadmium is a feebly exothermic process. Let us take another instance, that of the reduction of a solid oxide such as alumina.

The combination of this with oxygen gives an amount of energy which has not hitherto been measured directly, but the heat of formation of the colloidal hydroxide is known, and it must be accepted as being somewhat

* F. O. Doltz and C. A. Grammann, ' Metallurgie,' 1906, vol. 3, p. 212, also pp. 372—375.

greater than that of the oxide, but only slightly greater. It is expressed by the following equation :—

$$\xi(2Al + 3O + xH_2O = Al_2O_3 . xH_2O) = 393 \text{ K}°.$$

All attempts to reduce alumina by means of carbon alone, or carbon acting jointly with carbon monoxide on an industrial scale have failed, though many such processes have been devised.

The fact may be accounted for by the following equations :—

$$\xi Al_2O_3 = 393 \text{ K}° \quad \text{or} \quad \xi\tfrac{1}{3}Al_2O_3 = 131 \text{ K}° \text{ endothermic ;}$$

$$\xi(2Al_2O_3 + 3C = 4Al + 3CO_2) = -495 \text{ K}°.$$

or, for 1 atom of oxygen removed, -82.5 K°.

Substituting for solid carbon, gaseous hydrogen, we have

$$\xi(\tfrac{1}{3}Al_2O_3 + H_2 = \tfrac{1}{3}Al_2 + H_2O) = -72.9 \text{ K}°,$$
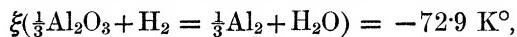
not a very great difference. Substituting gaseous carbon monoxide for solid carbon, we obtain

$$\xi(Al_2O_3 + 3CO = 2Al + 3CO_2) = -188.1 \text{ K}°,$$
$$\quad\;\; 393 \qquad\qquad\qquad 68.3 \times 3$$
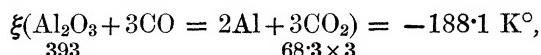
or, for 1 atom of oxygen removed, $\tfrac{1}{3}$ of this $= -62.7$ K°.

The actual energy supplied in these reactions before the aluminium can be reduced is for carbon, carbon monoxide, and for hydrogen respectively, -82.5 K°, -62.7 K°, and -72.9 K°. The carbon monoxide value is thus shown to be less than that in either of the other two reactions. It has already been proved, first, that alumina is reduced to the metallic state in the oxyhydrogen flame ; secondly, that the reduction takes place more easily when the alumina is mixed with some dense form of carbon. In the first instance, the flame alone supplied hydrogen only as the reducing agent, consequently, the energy required for every atom of oxygen removed was 72.9 K° in the form of extraneous heat which was necessary not only for initiating the process, but also maintaining it. When solid carbon was used, this was a somewhat higher figure, being 82.5 K°, but this very reduction process with solid carbon would result in the formation of carbon monoxide which could then operate upon another molecule of alumina, which places the extreme limits of the energy required for reduction as between 63 K° and 82.5 K°. From this it would appear that *any reducing process may be carried out in the oxyhydrogen flame by a purely chemical action if the extraneous energy required to initiate and maintain the action does not exceed** 84.8 *K° per atom of oxygen to be removed.*

* This is the figure for the zinc reduction $\xi ZnO = 84.8$ K°, that calculated for alumina is 82.5 K°.

Let us now consider another instance of the reduction of a solid oxide in the flame, namely, beryllia.   The energy of formation of the oxide is unknown, but its composition is BeO.

Pollok has measured the heat of formation of the chloride $\xi BeCl_2 = 155$ K$^\circ$, and of the heat of dissolution of beryllium in aqueous hydrochloric acid $\xi BeCl_2 = 199 \cdot 5$ K$^\circ$.   Comparing these results with the heat of formation and solution of aluminium chloride, we obtain the following figures:—

	Al_2Cl_6.	$\frac{1}{3}Al_2Cl_6$.	BeCl.
Heat of formation	323·6	107·9	155·0
Heat of solution............	152·6	50·9	44·5

Similar comparisons, made with magnesium and zinc chlorides, give

	$BeCl_2$.	$MgCl_2$.	$ZnCl_2$.
Heat of formation	155·0	151·0	97·4
Heat of solution............	44·5	36·0	15·6

These figures show that in each case a fall in the heat of formation and solution accompanies the rise in the atomic weights.

Now $\qquad\qquad \xi Al_2O_3 = 393$ K$^\circ = \xi\frac{1}{3}Al_2O_3 = 131$ K$^\circ$,

and $\qquad\qquad\qquad \xi\frac{1}{3}Al_2Cl_3 = 107 \cdot 9$ K$^\circ$,

the difference, 23·1 K$^\circ$, shows that the energy of formation of the oxide is by that amount greater than the chloride, and as

$$\xi BeCl_2 = 155 \text{ K}^\circ,$$

we may assume the value

$$\xi BeO = 178 \cdot 1 \text{ K}^\circ$$

to be approximately correct.   But

$$\xi MgO = 143 \cdot 4 \text{ K}^\circ \quad \text{and} \quad \xi ZnO = 84 \cdot 8 \text{ K}^\circ,$$

also $\qquad \xi MgCl_2 = 151 \cdot 0$ K$^\circ$ and $\xi ZnCl_2 = 97 \cdot 4$ K$^\circ$,

the difference between magnesium chloride and oxide is 7·6 K$^\circ$ and between zinc chloride and oxide 2·6 K$^\circ$, we may assume then that $\xi BeO = 148$ K$^\circ$, and this number is very probably more correct than that derived from the figures obtained from a comparison of the difference between the oxide and chloride of aluminium, because magnesium and zinc belong to the same group as beryllium, and aluminium does not.

The metal is certainly reduced from the oxide by the oxyhydrogen flame, and, as far as we know, beryllia is not a volatile oxide, nor is it fusible.   The reduction must, therefore, be the result of a purely chemical action, and it must also be of a highly endothermic character, as may be seen by the equation following:—

$$\xi (BeO + H_2 = Be + H_2O) = -97 \cdot 4 \text{ K}^\circ.$$
$$\quad\; 148 \qquad\qquad\qquad 50 \cdot 6 \quad \text{Endothermic.}$$
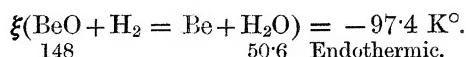
It may be inferred from the evidence afforded by the flame spectra, that at these high temperatures the infusible and non-volatile metallic oxides are in a peculiarly active condition, having absorbed a large amount of energy from the flame, so that they are approaching the condition of dissociation and are, therefore, subject to chemical interactions with the reducing gases, which otherwise would have no power to reduce them.   But in the cases referred to, the reducing gas is hydrogen, and in all probability it is not the hydrogen supplied to the flame in the molecular condition, but hydrogen in the atomic or nascent state, resulting perhaps from the dissociation of water, the product of combustion in another part of the flame, which carries with it the additional charge of energy which enables it to initiate and complete the reduction process.

Conclusions.

(1) The oxides of calcium, strontium, and barium, are not dissociated by heat alone, because they show no spectrum in a carbon monoxide flame; (2) They are reduced by the combined action of heat and hydrogen in the oxy-hydrogen flame and by the action of cyanogen in the cyanogen flame; (3) The flame coloration is due to the metal, because not only is the flame spectrum from lime essentially the same as that of the metal calcium, but also the heats of formation of CaO, SrO, and BaO have very nearly the same value, and that where calcium oxide can be reduced the other oxides could, on that account, undergo a similar reduction.   Whether the compound of strontium or barium in the flame be a sulphide or an oxide, the same spectrum is emitted, but there is some uncertainty as to whether the barium sulphide is not converted into oxide by water-vapour in the flame.

The explanation given by Lenard, of the flame coloration by the alkali salts, appears to be inapplicable to the coloration of the carbon monoxide flame by the haloid salts of the alkaline earth metals.